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13. ABSTRACT *(Maximum 200 words)*

This research program aimed to achieve a better understanding of pyrometallurgical reactions during welding and process-microstructure correlations. The validity of proposed mechanisms for the formation of weld metal acicular ferrite was tested by using selected surrogate additions with similar chemical behavior but different physical properties compared to titanium-boron additions known to promote acicular ferrite formation. The results suggest that inclusion density and size distribution are the most important factors in acicular ferrite formation.

The evolution of inclusions in the weld pool during welding and solidification was modeled. Procedures are reported for the use of shielding gas oxygen content as a welding parameter to optimize weld metal microstructure and properties. Exothermically-assisted shielded metal arc welding consumables were evaluated as a possible means to substitute chemical energy for traditional electrical energy during welding. Exothermic reactions produced up to 40 pct. of the heat required for welding. The influence of electrochemical reactions during welding on weld metal composition was investigated. Evidence of electrochemical behavior in specific welding parameter ranges was found. A search for new non-destructive evaluation techniques and associated procedures to measure specific weld metal compositions or constituents was undertaken. As a demonstration, magnetic property measurements were used to detect phase transformations in Al-Cu alloys.

14. SUBJECT TERMS Welding Pyrochemistry, Process-Microstructure Correlations, Exothermically-Assisted Welding Consumables, Acicular Ferrite, Electronic and Magnetic Phase Detection, Structure Evolution

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PYROMETALLURGICAL, PHYSICAL, AND MECHANICAL BEHAVIOR OF WELDMENTS

Final Report

David L. Olson and Robert H. Frost

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Colorado School of Mines

4A. STATEMENT OF THE PROBLEMS STUDIED

This research program aimed to achieve a better understanding of pyrometallurgical reactions during welding and process-microstructure correlations. The validity of proposed mechanisms for the formation of weld metal acicular ferrite was tested by using selected surrogate additions with similar chemical behavior but different physical properties compared to titanium-boron additions known to promote acicular ferrite formation. The results suggest that inclusion density and size distribution are the most important factors in acicular ferrite formation.

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4B. SUMMARY OF THE MOST IMPORTANT RESULTS

Research efforts during this contract have concentrated on: (1) the influence of Zr-Al and Ti-B additions on the formation of weld metal acicular ferrite; (2) the prediction of the nature and formation sequence for nonmetallic inclusions in the weld metal; (3) the use of shielding gas oxygen as a welding parameter; (4) the development of exothermically assisted welding consumables; (5) the influence of electrochemical reactions on arc welding processes with a plasma electrolyte; and (6) the use of electric and/or magnetic detection and characterization of weld metal microstructure. The research activities are to achieve a better understanding of the pyrometallurgical reactions occurring during welding and to establish a better understanding of process-microstructure correlations.

Zr-Al and Ti-B Additions:

A project evaluating the various proposed mechanisms for the formation of weld metal acicular ferrite, the desired high toughness-higher strength microstructure, was completed. By using surrogate additions the research found that low ferrite-inclusion lattice mismatch is not a primary factor as suggested by other investigations [1B-7B]. The important factor in controlling the weld metal microstructure, and thus the properties, was found to be the inclusion number density and size distribution [8B-11B]. The work indicated that Zr-Al microadditions to the weld pool can achieve the same weld metal microstructure and properties as commercially-used Ti-B microadditions. Zirconium was selected to replace titanium because it is chemically similar to titanium but has oxides with very different lattice mismatch compared to ferrite. Aluminum was selected to replace chemically similar boron to allow comparisons of their results. In small

concentrations, aluminum behaves like boron. The substitution of zirconium and aluminum for titanium and boron thus allowed evaluation of the validity of various models for the microstructural evolution of weld metal microstructure. Since the results suggested that inclusion density and size distribution are primary factors, it became apparent that inclusion evolution needs to be thoroughly understood in order to establish new effective ways to formulate high performance welding consumables.

Sequence of the Evolution of Inclusions:

A precipitation sequence model was developed which used the free energy of formation of various oxides and a model for microsegregation of alloy elements and oxygen during weld solidification to predict the location (weld pool or interdendritic) and the order in which the inclusions formed [12B, 13B]. For aluminum-killed steel with titanium microadditions this model predicts that aluminum oxide inclusions will be the first to precipitate and that these inclusions will continue to form during the initial stages of solidification. Ti_2O_3 and Ti_3O_4 inclusions will form near the end of solidification, and manganese and silicon oxides will only form during the final stages of solidifications. The sequence of oxide formation, when considering both the various temperatures of oxide formation and the interdendritic microsegregation, was found to explain the often observed bimodal size distribution. The larger inclusions result from the primary deoxidation, the role of the aluminum addition; and the much smaller inclusions result from the compositional perturbations found in the interdendritic regions and from the much lower formation temperature common to the interdendritic regions. The work suggests that weld metal microstructural optimization will result from proper selection of alloy additions and specifically selected shield gas oxygen content.

Shielding Gas Oxygen Content as a Welding Parameter:

An investigation was performed on microalloyed steels to demonstrate that weld metal microstructures can be altered by small shifts in the shielding gas oxygen content. The results showed that weld metal microstructure and properties can be optimized by use of simple metallographic determination of the fractions of the various forms of weld metal ferrite for a specific shielding gas oxygen content [14B-16B]. The shielding gas oxygen content can then be varied by a known amount to achieve a more desirable weld metal microstructure. The relationship between weld metal oxygen content and the oxygen or carbon dioxide content in the shielding gas was determined. The work furthered the predictability of weld metal microstructure and properties by developing a modified P_{cm} alloying index to include weld metal oxygen content [17B]. This index is called the P_{cmo}.

Exothermically Assisted Welding Consumables

The possibility of producing a chemically self-heating welding electrode was investigated. A liquid nitrogen calorimeter was used to study the heating effects of exothermic additions to flux-coated welding consumables during shielded metal arc welding. The calorimetry data was studied in conjunction with weld bead area measurements to correlate the heating effect with the melting of the base plate and electrode. The exothermic additions evaluated consisted of aluminum/hematite, magnesium/hematite, and aluminum/magnesium/hematite mixtures. All three types of additions were found to increase the amount of heat transferred to the work piece. Exothermic reactions produced up to 40 percent of the total heat required for shielded metal arc welding.

This investigation has shown that exothermic welding consumables can assist in heat generation and electrode melting [18B]. Aluminum additions are significantly more effective than magnesium in melting the electrode and weld bead, and in promoting increased penetration of the base plate. Magnesium is less effective in supplying heat because its reaction rate is high compared to the rate of electrode melting. The resultant prematurely-evolved heat cannot be transferred effectively to the base plate. It is desirable to have most of the exothermic reactions occur in the molten electrode tip, and to transfer the heat to the base plate via the molten droplets. The relationship between the rate of the exothermic reaction and the melting rate of the electrode determines the overall efficiency of the process.

Present efforts have progressed from shielded metal arc welding to evaluation of the use of cored wires that contain exothermic additions. The cored wire consumables should increase the thermal efficiency of the process and allow for more of the required heat to be generated by chemical reactions. The use of cored wires to achieve exothermic assisted welding consumables will be continued with a follow-up ARO contract (DAAH04-95-1-0135). A strip-to-cored wire mill has been procured and is being set up for experimental cored wire production.

<u>Influence of Electrochemical Reactions during Welding</u>:

Efforts to determine the influence of electrochemical reactions have investigated reactions involving the plasma in the shielded metal arc welding process [19B-23B]. During shielded metal arc welding current is transferred across both the plasma-metal and slag-metal interfaces. The charge carriers in the plasma include electrons and positively ionized atoms, but negative ions such as those found in molten slag conductors are not available. Composition changes at the

plasma-metal interface are controlled by the nature of the charge carriers in the plasma and by vaporization from the metal surface to the plasma.

Direct current shielded metal arc welds were made on a copper plate in both DCEP and DCEN polarities. The nature and extent of electrochemical reactions were investigated as a function of polarity, current, and weld travel speed by chemical analysis of the weld bead, the electrode tip and of the metal droplets. The compositional changes in these specimens provided information on the electrochemical and thermochemical processes at the electrode, on the thermochemical reactions during droplet transfer and on the back chemical reactions in the weld pool as the weld pool tries to reestablish equilibrium.

Comparative studies were made of composition variations seen during SMA and SA welding. The results show that there are differences in the electrochemical reactions at slag-metal and plasma-metal interfaces. Conduction at slag-metal interfaces is primarily ionic, and both positive and negative ions are present in the slag. For example, oxygen reactions at the slag-metal interface include oxygen discharge and pickup at the anode and oxygen refining at the cathode:

Slag-Metal Interface

Anode: $(O^{2-})_{slag} = [O]_{metal} + 2e^-$

Cathode: $[O]_{metal} + 2e^- = (O^{2-})_{slag}$

The electrochemical reactions are different at the plasma-metal interface, because only positive ions exist in large concentrations in the plasma. This results in oxygen refining at the anode and oxygen pickup at the cathode:

Plasma-Metal Interface

Anode: $[O]_{metal} = \{O^+\}_{plasma} + e^-$

Cathode: $\{O^+\}_{plasma} + e^- = [O]_{metal}$

These reactions show that the absence of negative ions in the hot plasma causes the chemical influence of electrochemical reactions to be in opposite directions at the plasma-metal and the slag-metal interfaces.

The experimental results show further that the welding current and the weld travel speed are both important process variables. The results show that the plasma/metal interface controls the electrochemical transfer of metallic elements, and the slag/metal interface controls the electrochemical transfer of nonmetallic elements such as oxygen and sulfur. The anodic electrochemical reactions include the oxidation of iron and alloy elements at the plasma/metal interface and the discharge and pickup of nonmetallic anions such as oxygen and sulfur through the slag/metal interface. The cathodic electrochemical reactions include the reduction of iron and alloy elements through the plasma/metal interface and the refining of nonmetallic elements through the slag/metal interface. The extent of both anodic and cathodic reactions increased as the welding current increased and as the weld travel speed decreased.

Electric and Magnetic Detection and Characterization of Microstructure Constituents:

Electric and magnetic measurements of weldments may serve as a method to determine carbide types and content in steel, phases in aluminum, hydrogen content in steel and other constituents that influence the performance and service of weldments. This investigation demonstrated that measurements of bulk magnetic properties can quantitatively determine the

precipitation sequence (GP1, GP2, Θ', and Θ) in aluminum-copper alloys [24B, 25B]. The ability to characterize alloy properties and phase stability through correlations with electromagnetic measurements may allow significant improvements in the nondestructive evaluation of advanced alloy properties and the prediction of service life.

4C. LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

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1. David L. Olson, Co-Principal Investigator
2. Robert H. Frost, Co-Principal Investigator
3. Jeffrey W. Allen, M.S. Student (completed June 1994)
4. Dong. W. Oh, Ph.D. Student (completed December 1992)
5. Jong H. Kim, Ph.D. Student (completed March 1993)
6. David Fleming, M.S. Student (assisted with review article on welding flux)
7. Wesley Wei Wang, Ph.D. Student
8. Steven Malene, Ph.D. Student
8. Jose Ramirez, Post-Doctoral Scientist

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